

FROM ONE EXTREME TO THE OTHER: USING FUNDAMENTAL CHEMISTRY TO  
UNDERSTAND COAL BEHAVIOR OVER WIDE RANGES OF CONDITIONS

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Efforts to understand coal chemistry at a fundamental level face a good deal of complexity and uncertainty, but can also lead to major simplifications. Certain fundamental ideas have very broad applicability and can unify seemingly divergent aspects of coal behavior. Three such cases will be discussed. 1) With increasing coal rank and coal processing severity, increasingly strong bonds are broken. An overview of the "scissile" (weak) bonds present in coal and the conditions under which they cleave will be discussed, covering conditions from geothermal processing to fast coal pyrolysis. 2) While the chemical details of condensation reactions of polyhydroxy-benzenes are not entirely clear, these reactions cannot be avoided and it is probable that they determine the chemical properties of higher rank coals and underlie char-forming reactions in coal processing. A discussion of some of the implications of these reactions for coal chemistry will be presented. 3) Theoretical results suggest remarkably little dependence of the thermochemistry and free radical kinetics of polycyclic aromatic hydrocarbons (PAHs) on molecular size. This can lead to a considerable simplification in the analysis of coal char chemistry.

1) Simple Bond Breaking

Chemical bond dissociation follows a first-order rate law with the rate constant:

$$k_{\text{break}}/\text{s}^{-1} = 10^{15.0 \pm .1} \exp(-\text{Bond Dissociation Energy}/RT)$$

Given a characteristic time,  $t$ , for which the temperature  $T$ , has remained constant, bonds weaker than some bond strength  $\text{BDE}(T, t)$  will be unstable towards dissociation. For coal, characteristic times range from geologic ages ( $10^8$  years or  $10^{15}$  sec) to fast coal pyrolysis ( $10^{-3}$  sec) and temperatures from ambient to over 600 C. The types of bonds in coal with these characteristics will be pinpointed and discussed. They span the rather narrow range of bond strengths from 50 - 65 kcal/mol and include most varieties of alkyl-aryl ethers and 1,2-diarylethane linkages. The most significant scissile bonds in the thermal processing of coal are those just strong enough to have resisted dissociation under geothermal conditions.

## 2) Polyhydroxy aromatics

Studies of the reactions of dihydroxy-aromatic compounds by McMillen [1] and ourselves [2] demonstrate that at under conditions characteristic of coal liquefaction, these substances are almost entirely transformed into polymeric materials. Since the ortho hydroxy/alkoxy structure is the characteristic reactive unit in lignin and, presumably, in low rank coals and since these will ultimately form dihydroxybenzenes through dissociation pathways under coalification and coal processing conditions, these reactions are probably may be of central importance in the formation of high rank coals and char. A discussion of features of these reactions that are known and unknown will be presented.

## 3) Polycyclic Aromatic Hydrocarbons

These are characteristic products in the pyrolysis of virtually all hydrocarbons and are predominant in char and probably in anthracite coal. Theoretical studies [3] indicate that the edges of very large PAH clusters have chemical properties very similar to those of conventional and well-studied PAHs. Even at the edges of a layer of graphite properties of chemical structures depend very little on the long-range network of pi-electrons—instead individual sites behave in a manner similar to similar sites on convention PAHs. These "active sites" are the centers of reactions in both combustion and gasification.

## References:

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- 2) S.E. Stein, Accounts of Chemical Research, 24(11), 250 (1991).
- 3) F.M. Wang, V.P. Senthilnathan and S.E. Stein, Proceedings of 1989 International Conference on Coal Science, Tokyo, Japan, 1989, 165-168.